GUIDANCE DOCUMENT FOR THE ELEMENTAL CHARACTERIZATION OF LIQUID WASTE SAMPLES

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Prepared by:
Laboratory Services Branch
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Guidance Document for the Elemental Characterization of Liquid Waste Samples

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INTRODUCTION

A key component of the Municipal/Industrial Strategy for Abatement (MISA) program is the development of a comprehensive database of contaminant discharges to surface waters in Ontario. During the initial phase, direct discharges from major industrial and municipal sources are to be sampled and analyzed for the concentrations of a number of substances in order to characterize these effluent streams. MISA regulations[1] require periodic sampling and analysis at prescribed intervals for an ongoing assessment of rates of discharge, effects of abatement measures, etc., supported by random monitoring by the Ministry of the Environment (MOE). Additional information describing the analytical parameters of interest can be found in the MISA Effluent Monitoring Priority Pollutants List (EMPPL)[2].

This document presents an overview of the analytical approach adopted by MOE Laboratory Services Branch, to meet the analytical needs for monitoring elemental parameters. For a few parameters, additional special techniques are required but these are not described in detail. Since this document is a guideline, not a formal analytical method, the description simply highlights the features of the approach. It should not be used as a procedure for analysis of MISA samples. If more detailed information is required then requests for the current method write ups should be made to the Quality Assurance Office of the Lab Services Branch[3].

1. Analytical Approach

Analytical methodologies are traditionally described as qualitative, semiquantitative, or quantitative.

Qualitative methods are employed to detect the presence or absence of analytes in a sample.

Quantitative methods are the most precise and accurate. An overall accuracy of up to 10% to 15% may be acceptable for any given determination, although better accuracy is certainly desirable and frequently achieved. The application of quantitative methods is limited to samples whose major composition does not change significantly. In such a case a method can be designed in such a manner so as to be specific for the desired analytes and so that sources of error can be identified and minimized or eliminated. Note that this is only possible if the overall compositions of the samples are well known. If the compositions of the samples are highly variable, (as with MISA industrial effluent), it becomes impossible to develop a single method which is quantitative for all analytes in all samples. This is mainly due to the fact that if the overall composition of a particular sample is unknown then it is not possible to identify and correct for possible interferences.

An additional factor in the development and designation of an analytical method is that of peer review. The time and expense associated with the certification of a method is considerable. In some cases it takes years before a method is accepted as "standard" or "official".

Semiquantitative methods fall between these two approaches. Higher overall uncertainties in the final results may be tolerable, compared to a result from a quantitative method, but the final product is still a numerical result with an associated uncertainty. Semiquantitative methods are rarely peer reviewed and thus do not provide the assurance that these methods offer.

Given the variety of municipal and industrial sources of pollutants in the province, the development of a single quantitative method for the characterization of all of the possible industrial effluent streams in Ontario is not practical and most methods that are applied to characterization of

industrial effluent are designated as being semiquantitative.

2. Elements of Interest

In addition to hydrogen and oxygen, water has 10 principle constituents[4,5,6]: Ca Mg Na K C N Si P S Cl.

Another 28 elements are typically detected in water at low concentrations: Li Be B F Al V Cr Mn Fe Co Ni Cu Zn As Se Br Rb Sr Mo Ag Cd I Cs Ba Hg Pb Ra U.

Thirteen elements normally occur at extremely low concentrations, except when their concentrations are elevated by pollution: Ti Ga Ge Zr Pd In Sn Sb Te Ta W Tl Bi.

Other elements are generally not detected by current analytical methodology but may be found at elevated levels in industrial effluent.

Ministry methods can determine the concentrations of 70 elements: Al Sb As Ba Be Bi B Cd Ca Ce Cs Cr Co Cu Dy Er Du Gd Ga Ge Au Hf Ho In Ir Fe La Pb Li Lu Mg Mn Hg Mo Nd Ni Nb Os Pd P Pt K Pr Re Rh Rb Ru Sm Sc Se Si Ag Na Sr S Ta Te Tb Tl Th Tm Sn Ti W U V Yb Y Zn Zr. These are the elements specified in the MISA General Regulation as Analytical Test Group 29.

3. Available Techniques

The Ministry of the Environment has developed a set of methods using various techniques including plasma source emission spectroscopy, plasma source mass spectrometry, flame and flameless atomic absorption spectroscopy.

Alternate techniques which are available but are not generally utilized by the Ministry for characterization of aqueous effluent are: polarography and other electrometric techniques, ion chromatography, colorimetry, fluorometry, neutron activation analysis, energy and wavelength dispersive XRay spectrometry, and proton induced XRay spectrometry.

Other techniques, such as electron microscopy with ion microprobe, are capable of excellent sensitivities but are more appropriate for analysis of surfaces or of individual particles, rather than determination of the total elemental content of aqueous samples.

No single technique can be recommended and many practical concerns should be considered when selecting techniques for use when developing methods for the analysis of industrial wastes. Sample throughput for the single element techniques has been increased through technological advances such as microcomputer controllers, and flow injection apparatus.

Multielement techniques are preferred because of the number of parameters to be measured. However, there are some cases where inadequate performance characteristics preclude their use and single element techniques must be used to develop methods.

Practical concerns such as instrument availability, capital and operating costs, laboratory space, the availability of trained personnel, etc., are also important factors in selecting a technique for developing a routine method.

The following discussion applies particularly to plasma source emission spectroscopy and plasma source mass spectrometry but the general approach would be similar with any technique. The discussion presents an overview of optical emission spectroscopy and mass spectrometry, particulary those characteristics which are relevant to the analysis of MISA samples.

Methods based on plasma techniques are used for most of the elements required to be characterized by MISA because they are sensitive, multielement, and relatively specific. These instruments are employed in most laboratories, have had wide application to a variety of sample types, and form the core of MOE methods for elemental characterization.

BASIC PRINCIPLES OF PLASMA-SOURCE EMISSION AND MASS SPECTROSCOPY

1. Development Plan

Development of a spectroscopic analytical method includes many steps:

- selection of elements to be analyzed
- estimation of the concentration range expected for each analyte
- selection of analytical wavelengths or isotopes
- optimization of instrument parameters
- determination of detection limits
- verification of the linearity of the response curves
- preparation/acquisition of calibration and standard solutions
- optimization of method parameters
- examination of inter-element effects (spectral overlap or coincidence)
- determination of precision (short term; long term)
- establishment of Quality Assurance/Quality Control protocols
- method validation (analysis of standard reference materials, duplicate samples, spiked samples;interlaboratory comparisons)
- data handling and reporting procedures
- method write-up

Development of a suitable sample preparation procedure may take place concurrently.

The development is usually an iterative, rather than a linear process. For instance, in emission spectroscopy it is desirable to use the most intense emission line for each element, as might be found in line libraries[7], so that the highest sensitivity can be achieved. However, later examination of interelement effects may show significant interferences by some elements and a less sensitive interference free wavelength may be substituted. Alternatively, a numerical correction factor may be calculated to remove the interelement interference. The same may be said for using the most abundant isotope of an element to obtain the best detection limit in mass spectrometry.

2. Sample Preparation

In most cases, a sample preparation step is necessary before introducing the sample into the analytical instruments. Strictly speaking, most methods based on plasma techniques are applicable only to single phase liquid waste samples; ie, the samples either do not contain any solid material, or the solid material present in the samples has been decomposed by suitable digestion procedures.

Some liquid industrial wastes discharged into surface waters contain solid phase material in addition to the predominant liquid phase. A digestion is necessary before analyzing such samples for the total element content. Experience at the MOE laboratory has led to a three group sample classification:

Type 1 • clear, coloured, some sediment
Type 2 • oily, sludge, hard to digest
Type 3 • clear, colourless

Type 1 samples are digested with a combined thermal/acid treatment. The treatment is carried out in two steps, the first with concentrated nitric acid,

and the second with aqua regia with heat supplied by a hot plate.

Type 2 samples are ignited in a muffle furnace before carrying out a thermal/aqua regia digestion. For some analytes it may be necessary to use an ashing aid or to employ sealed bomb digestion vessels with heat supplied by either microwave or conventional ovens. Both types of samples are readied for introduction into the analytical instrument by diluting to a fixed volume with doubly distilled water.

Type 3 samples can be usually be filtered, checked for conductivity and run directly into the nebulizer of the spectrometer.

3. Plasma Excitation Sources

There are two main analytical techniques that rely upon plasmas: plasma source optical emission spectrometry and plasma source mass spectrometry.

Plasma source emission spectroscopic techniques use high energy plasma sources to excite the analyte atoms in the sample. A plasma can be defined as a hot ionized gas that achieves estimated temperatures above 6000 K. Subsequent relaxation of the atoms is accompanied by the emission of photons of light with a characteristic wavelength (ie a characteristic energy). Each element has a number of these emission lines, the exact wavelengths depending on the atomic structure of the element. It is the wavelength (energy) of the light emitted that is used to identify what element is present. The intensity of the light at a particular wavelength is proportional to the number of atoms excited and therefore is directly related to the concentration of the element in the sample.

Thermal flames are sufficiently energetic to excite some easily ionizable elements such as sodium but plasma sources achieve much higher temperatures. This allows them to excite a much wider range of elements and helps to reduce matrix effects at least for atomic emission. Two types of plasma sources are commercially available at present: direct current (DCP), and inductively coupled RF plasma discharges (ICP).

The aqueous sample extract is most commonly introduced into the plasma discharge through a nebulizer, which produces a fine aerosol mist that is carried into the plasma through a spray chamber by an inert gas stream. The DCP is considered somewhat more robust in that it can tolerate higher sample loadings, but long term precision may be degraded by wear of the electrodes.

Plasma source mass spectrometry utilizes the ions produced in the plasma. Elements are detected by separating a particular mass of ion(s) of the monitored analyte. In this case it is the number of ions produced per second for a particular mass that is directly related to the concentration of the element in the sample. Details can be found in standard texts[8].

4. Spectrometers

a) Emission Spectrometers:

The light from the plasma discharge is directed into an optical spectrometer, which is designed to discriminate between photons of different wavelengths. Spectrometers fall into two general classifications, sequential and simultaneous (also referred to as monochromators and polychromators). There are advantages and disadvantages to each type.

A sequential spectrometer is cabable of measuring the intensity of light emitted at a number of wavelengths. It but does so by sequentially viewing one wavelength at at time. In many of these instruments a diffraction grating is used to separate the light from the plasma into the different wavelengths and a particular wavelength is selected for viewing by rotating the grating. The

advantage of a sequential instrument is that it is versatile. Several wavelengths can be scanned for each element to locate one that is of sufficient intensity and for which there is no interferences. The disadvantage is the time involved with this process which increases linearly with the number of elements measured.

Simultaneous spectrometers have a separate detector and electronics setting for each wavelength to be detected. The light is diffracted by an optical grating such that photons with different wavelengths are distributed along an arc. The detectors are located along the arc at specific positions; the physical size of the spectrometer can thus be a limiting factor. However, this type of spectrometer determines all of the analytes in the sample at the same time thus maintaining a high sample throughput. The disadvantage is that, for most of these instruments, the configuration of the detectors is set for certain lines of the target elements at the time of installation and cannot easily be altered. Thus they are not as versatile as the sequential instruments are.

b) Mass Spectrometers:

A mass spectrometer detects the positive analyte ions formed in the plasma. Ions are extracted by a specially designed interface which forms an ion beam suitable for introduction into the mass spectrometer. After passing through a series of ion lenses, the ion beam is focused into a quadrupole mass spectrometer. The quadrupole or "mass filter" selectively passes positive ions of interest and "blocks" all others. Positive ions passing through the quadrupole are then detected by a channel electron multiplier. A pulsed signal from the channel multiplier is fed into appropriate signal handling electronics and converted for computer use.

The ion lenses, quadrupole and detector are all housed in a chamber which is evacuated to $1x10^{-5}$ torr by a cryogenic pump for efficient ion transmission and detector operation.

The output from the computer reports the number of ions impinging on the detector in one second (intensity). This intensity is proportional to the concentration of the analyte in the liquid sample and with an appropriate calibration curve, the computer calculates the final answers in mg/L.

c) Additional considerations:

The importance of instrument flexibility cannot be overstated when dealing with complex and variable sample matrices such as industrial effluent. Anomalous results can be checked by repeating the analysis using another analytical line or isotope, or by scanning through a wavelength or mass region and visually examining the results for unusual peaks or background shifts.

When working with samples of variable and unknown composition high resolution spectrometers are required for accurate work. Resolution refers to the capability to discriminate between closely spaced analytical wavelengths (lines). Higher resolution is normally required for complex sample matrices such as industrial wastes, which have a large number of analytical lines, than is required for simpler sample matrices such as drinking water. While concentrations are lower in the latter type of sample, requiring a higher sensitivity, the optical or mass spectrum is simpler and likely to have fewer overlapping lines or isotopes than the spectra from industrial waste samples.

An additional consideration is whether the emission spectrometer chamber should contain air, be purged with inert gas, or be under vacuum. Because oxygen strongly absorbs light at wavelengths less than 200 nanometres, purged or evacuated systems are necessary for the measurement of analytes such as sulphur at these low wavelengths.

5. Biases and Interferences

Biases and interferences arise from a number of sources. Samples must be collected according to established protocol, in approved containers, and with any necessary preservatives added in the correct amounts; otherwise, results from the analytical laboratory will be invalid. Chemical biases can be introduced by contamination or by a digestion procedure which recovers less than 100% of each analyte of interest. Both of these biases may exist in the preparation of industrial waste samples for spectroscopic analysis, and can limit the overall accuracy of the method.

Biases arising during routine analysis of samples can be controlled to within tolerable levels by incorporating a system of instrument blanks, reagent blanks, composite standards of known composition, analysis of duplicate samples, etc. The MISA regulations [1] include a specific QC run protocol for analysis of liquid waste samples by private laboratories. Most Ministry methods go beyond this protocol and include quality control procedures that are designed to detect the presence of sources of determinate error that are unique to the specific method.

When using emission spectroscopy a spectral bias can occur when the background intensity in the region of an analytical line differs between standard and sample. The bias can be removed by applying a background correction: the concentration of an analyte is determined not from the intensity at the analytical wavelength alone, but from the net intensity calculated as the difference in intensities between the analytical wavelength and a wavelength offset from the analytical line. The offset is usually visually selected so that it is in a region that does not include any significant emission lines. Either a 1 point correction or a 2 point correction can be applied; 2 point corrections are necessary when the background intensities on either side of the analytical line do not change by the same amount.

Both emission and mass spectrometries suffer from spectral interferences which are caused by overlapping of lines or isotopes from different elements. In emission spectrometry, when a wavelength region is scanned and examined visually, the intensities from the analytical wavelengths do not appear as discrete lines, but rather as peaks with a finite width. Closely spaced peaks may overlap to give a composite peak, or if sufficiently close, may appear as one single peak. The ability to separate peaks depends on the resolution of the spectrometer. If an analytical line cannot be fully resolved from a neighbouring interfering line, then an interelement interference is present. A correction factor can be determined by analyzing standards with a known concentration of the interfering element, and recording apparent concentration at the analyte line of interest. The concentration of the interfering element can then be determined in samples (using an alternate wavelength), and the amount of the interference can be calculated and subtracted from the original analyte line. Note that when this occurs the process removes the determinate error but leaves behind a residual indeterminate error (variance). This results in a method that has variable Lower Limits Of Reporting from sample to sample depending upon the relative concentrations of analyte and interferent. Since the intensities (and their associated variances) are known for both the analyte and for all interferences it is possible to estimate the uncertainty associated with each concentration estimate. These calculations should be carried out by the computer on the spectrometer and their affects should be communicated via appropriate remarks associated.

Such interferences have a significant effect on the accuracy of the final result. There is a larger error associated with a corrected concentration than with a result obtained in the absence of interelement interferences. This is because the corrected result requires three empirical measurements: the concentration of the target analyte, the concentration of the interfering analyte, and the interelement correction factor. There are uncertainties associated with each of these, which increase the uncertainty in the final corrected result. Standard

texts[9], can be consulted for a description of how errors propagate with each additional mathematical operation. Possible inter-element interferences should be examined for each analytical wavelength or mass; a list of potential interferences can be compiled by examining line or isotope libraries for strong lines or isotopes in the region of the desired analyte wavelengths or mass. The presence of any interelement interferences can then be verified experimentally.

Mass spectroscopy has far fewer spectral interferences than emission spectroscopy due to the nature of the ionic detection. However, isobaric interference does occur when an interfering isotope has the same mass as the analyte isotope. This interference is readily overcome by using elemental equation correction factors.

Another type of interference in mass spectroscopy is oxide formation. The formation of an oxide from a major constituent of the sample may produce ions of a mass that could interfere with the particular analyte mass monitored. This may be overcome by changing instrument set up conditions or monitoring an analyte isotope at a different mass.

A considerable error may be introduced by matrix effects, especially in mass spectrometry. These occur when the nature of the plasma discharge (or ion lenses in mass spectrometry), or the sample intake, is changed by the presence (or absence) of one or more elements. Matrix effects are reduced when the major constituents of the samples are at similar levels in the standards. It is not always possible, or desirable, to reproduce the matrix in this fashion. When the major constituents have different concentrations or are in different proportions, then the instrument response to a given concentration of an analyte is no longer identical for both samples and standards. Matrix effects are commonly encountered in solutions with high concentrations of salts or easily ionized species.

Different sample matrices should be expected when establishing a method for the analysis of effluent streams from many different sources. With a limited number of source types, the sample matrix may be sufficiently consistent that the method standards can be matched to it. For characterization of a variety of industrial source types, results should be closely screened before approval.

6. Method Validation

The preferred means of establishing the validity of an analytical method is to analyze a number of standard reference materials (National Bureau of Standards, Environmental Protection Agency, National Research Council of Canada, etc.) which are similar to the sample types expected, and which have certified concentrations of elements covering the range of method calibration for each element. Interlaboratory checks, round robbin participation, and audits are important ways of validating any method.

If there is no standard reference material matching the expected sample matrix, additional validation steps are needed. The simplest approach is to do a paired comparison with results from one or more established techniques. It is important to use a statistically significant number of samples in such a comparison, and to include both typical samples and samples which cover the entire concentration range of interest.

Method Detection Limits (MDL) must be determined to see whether the final method has sufficient sensitivity to meet the requirements of MISA. Standardized procedures[10] have been developed to derive these figures for each analyte. The existence of this MDL does not absolve the analyst from dealing with the effect of variable precision which is caused by the removal of known sources of determinate error, as outlined previously in this report. The analyst is responsible for reporting his results along with uncertainties and/or appropriate qualifying remarks.

Additional comparisons can be made using spiked samples. To verify the complete method, aliquots of elemental standards of known concentration can be added before digesting samples. Samples can also be spiked after digestion, but the results would normally be indicative of instrument performance only.

Anomalous results encountered during analysis can also be verified using spiking and/or dilution. If the analyst suspects an uncorrected interference, the sample can be reanalyzed after spiking with an appropriate amount of the suspected INTERFERING element (NOT the analyte). A result, for the analyte, which is statistically different from the first result indicates an interelement interference. Alternatively, if a matrix effect is suspected, the sample could be diluted and reanalyzed; after correcting for the dilution factor, there should be no statistical difference.

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